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PROCESS AND CATALYSTS FOR DEEP DESULPHURIZATION OF
FUELS

The present invention relates to a process for the deep oxidative desulphurisation of hydrotreated hydrocarbon mixtures boiling in the diesel range containing sulphur impurities, effected in the presence of an organic oxidant and a catalytic composition containing a completely amorphous micro and/or mesoporous mixed oxide comprising a matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides selected from transition metal oxides and Group IVA metal oxides are uniformly dispersed. Optionally boron and/or gallium oxides can be contained in the catalytic composition.

15 The process is carried in absence of added solvent. The oxygenated sulphur products obtained have higher polarity and/or molecular weight and they could be easily separated from liquid fuels, for example by distillation or by solvent extraction methods or by

20 selective adsorption.

In the hydrotreated hydrocarbon mixtures boiling in the diesel range (180-360°C), and in particular in LCO (light cycle oil) range, preferably containing less than 350 ppm S, the sulphur compounds are

thiophenic compounds, in particular dibenzothiophene (DBT), alkylbenzothiophene (alkylDBT), polyalkylbenzothiophene (polyalkylDBT).

The hydrotreated hydrocarbons mixtures derives from a 5 hydrotreating process, a well-known process whereby hydrogen is contacted with a hydrocarbon stream and catalyst to effect a number of desiderable reactions, including the conversion of sulphur compounds to hydrogen sulphide. The reaction product is then 10 separated into a gaseous hydrotreated effluent stream and thus effectively removed from the hydrocarbon product. Hydrotreating can readily reduce the level of several common classes of sulphur compound such as sulphides, disulphides, and thiols, present in refinery 15 products. Unfortunately, however, hydrotreating often fails to provide a treated product in compliance with the strict sulphur level targets demanded currently.

The so-obtained hydrotreated hydrocarbon mixtures , and in particular LCO cut, containing said sulphur 20 compounds most refractory to hydrogenation process, are blended in diesel fraction. The new proposed specifics on S amount in diesel is becoming more and more stringent (Environment Council Dep. Proposal

13.12.01). The foreseen specifics are diesel with S < 10 ppm and diesel with S < 50 ppm by the 2005, while only diesel with S < 10 ppm by 2009. Such specifics anticipate the previous requirements (S < 50 ppm by 5 the 2005 and S < 10 ppm by the 2010). The conventional processes to desulphurize fuels are based on catalytic hydrogenation, at relatively high pressure (30-80 bar) and temperature (270-330°C): the new restriction requires higher H₂ consumption 10 therefore higher H₂ production, H₂ recovery and purification, revamp of reactor to increase the catalyst volume while maintaining catalyst cycle life.

The necessity has therefore been felt for 15 identifying a catalytic system which, combined with suitable non hydrogenation process, diminishes the sulphur in the hydrocarbons boiling in the range of the diesel, in mild condition.

The use of Ti-catalysts as selective oxidative 20 catalysts in presence of suitable peroxides is known and microporous crystalline titanosilicates such as TS-1 and Ti-Beta can oxidise alkyl and aromatic



sulphides with high level of conversion to sulphoxides and sulphones (US 4410501, Chem. Comm., 84(1992), Catal. Lett., 39, 153-156 (1996), J.Mol.Catal.A, 11, 325 (1996)). Besides, Ti-Beta and 5 Ti-HMS can oxidise some thiophenic compounds to the corresponding sulphones using H₂O₂ as oxidant with the necessary presence of large amounts of acetonitrile as solvent (J.Catal., 198, 179 (2001), WO 0148119). Ti-HMS is a hexagonal ordered mesoporous structure 10 characterized by an X ray powder pattern showing a single broad peak: reflection (100).

To apply this selective oxidation process to the sulphur removal in liquid hydrocarbon fuels, the two phases system may cause serious difficulties in term 15 of additional step process for the separation of solvent / water phase. Other catalytic systems can be applied to sulphur compounds oxidation with inorganic or organic peroxides, such as ITQ-2 zeolite in the case of thiols in WO 0034181, or MCM-41 in the case 20 of thioethers in US 5783167. The MCM-41 is a hexagonal ordered mesoporous structure characterized by an X-ray powder pattern showing a three peak

(reflections (100), (110) and (200)), due to some "long-range" order. Ti-HMS and MCM-41 hysotherms are of Type IV without hysteresis loop; this can be attributed to the cylindrical pores, having the same
5 size of pore mouth and pore body.

In the case of sulphoxidation of large organic sulphur compounds as polyalkylDBT in a complex matrix like a hydrocarbons cut boiling in the diesel range some structural restrictions take place, relating to
10 the diffusion of molecules into catalyst pores.

We have now unexpectedly found that it is possible to desulphurize hydrotreated hydrocarbons boiling in the diesel range, at milder condition than those preferably used in the hydrogenation process and in unique organic
15 phase, up to very low S level (< 10 ppm), by means of an organic peroxide and a completely amorphous micro and/or mesoporous catalyst comprising an oxide matrix wherein one or more oxidative metal oxides are uniformly dispersed.

20 EP 492697, US 5049536 and US 5625108 disclose completely amorphous micro-mesoporous metalloc-silicates, called MSA , having a rather narrow

distribution of the pore dimensions (average diameter of between 20 and 40 Å, basic absence of pores with a diameter of more than 40 Å), surface area > 500 m²/g, pore volume of 0.4-0.8 ml/g.

5 EP 691305 and EP 736323 also describe the possibility of preparing micro-mesoporous metallo-silicates, called ERS-8, characterized by a narrow distribution of the pore dimensions with an average diameter of <40 Å, a pore volume of between 0.3 and 1.3
10 ml/g a surface area of between 500 and 1200 m²/g. The MSA are completely amorphous, their XRD spectrum from powders does not have a crystalline structure and does not show any peak. The ERS-8 are completely amorphous, their XRD spectrum from powders does not have a
15 crystalline structure, does not show any peak and has a widespread reflection at low angles , indicating a "short-range" order in the micro-mesoporous structure.
These materials of MSA or ERS-8 type consist of a
silica matrix in which one or more metal oxides are
20 possibly uniformly dispersed , wherein the metals are selected from transition metals or metals belonging to groups IIIA, IVA or VA of the Periodic Table.

EP 812804 describes an improved preparative method of the above metalloc-silicate compounds comprising the following steps:

a) preparing a mixture starting from a
5 tetraalkylorthosilicate, a C₃-C₆ alkyl alcohol or dialcohol, a tetraalkylammonium hydroxide having the formula R₁(R₂)₃N-OH wherein R₁ is a C₃-C₇ alkyl and R₂ is a C₁ or C₃-C₇ alkyl, optionally in the presence of one or more metal compounds , in which the molar ratios
10 are within the following ranges :

- alcohol/SiO₂ < or equal to 20;
- R₁(R₂)₃N-OH/SiO₂ = 0.05-0.4;
- H₂O/SiO₂ = 1-40
- metal oxides/SiO₂ = 0-0.02

15 b) subjecting this mixture to hydrolysis and subsequent gelation at a temperature of between 20°C and a temperature close to the boiling point of the alcohol or mixture of alcohols present;

c) subjecting the gel obtained to drying and
20 calcination.

We have now unexpectedly found and that is a first object of the present invention a process for oxidative

desulphurization of hydrotreated hydrocarbon mixtures which boil within the range of 180° to 360°C, containing less than 350 ppm of sulphur as thiophenic compounds, which comprises putting these mixtures in 5 contact, in the presence of an organic peroxide, with a catalytic composition comprising a completely amorphous micro and/or mesoporous mixed oxide which contains an oxide matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or 10 more oxidative metal oxides selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, and separating the obtained corresponding sulphur oxygenated products from the hydrocarbon mixture. The oxidative dispersed metal oxide can be 15 selected from oxide of Ti, V, Zr, Sn and their mixtures. The catalytic composition can optionally contain also boron and/or gallium oxides.

The organic peroxide can be an alkyl- or an aryl-hydroperoxide, or a dialkyl- or diaryl-peroxide, 20 wherein the alkyl or aryl groups can be the same or different, and preferably the organic peroxide is terbutyl hydroperoxide or cumyl hydroperoxide.

The completely amorphous mixed oxides useful in the process of the present invention are micro and/or mesoporous material, according to the terminology suggested by IUPAC Manual of Symbols and Terminology,

5 Appendix 2, Part I Coll., Surface Chem. Pure Appl. Chem., (1972), Vol.31, page 578, in which micropores are defined as pores with a diameter of less than 20 Å and mesopores are defined as pores with a diameter of between 20 and 500 Å.

10 The molar ratio between the oxide matrix (YO) selected from silica, alumina, ceria, magnesia and mixtures of thereof, and the dispersed metal oxide (MO), preferably selected from the oxides of titanium, zirconium, vanadium, tin, is between 5/1 and 300/1, preferably 15 between 10/1 and 200/1. When boron or/and gallium oxides are present the molar ratio between the oxide matrix and boron and/or gallium oxide is between 5/1 and 300/1.

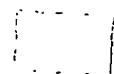
In the catalytic compositions useful in the process of 20 the present invention preferably the oxide matrix is selected from silica, alumina and mixture thereof, and the metal oxide is preferably selected from the oxides

of titanium, zirconium, vanadium, tin, and more preferably is oxide of titanium. When the oxide matrix comprises silica and alumina the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ is preferably ≥ 30 .

5 Completely amorphous microporous mixed oxides useful in the process of the present invention can be of AMM type, described in S. Klein, J. A. Martens, R. Parton, K. Vercruyse, P. A. Jacobs, W.F. Maier; "Amorphous microporous mixed oxides as selective redox catalysts", Catalysis Letters 38 (1996) 209-214.

10 The completely amorphous mesoporous mixed oxides useful in the process of the present invention can be prepared according with EP 748652, wherein one or more compounds, soluble in alcohol environment, of transition metals and/or group IVA metals are used.

15 The completely amorphous micro-mesoporous mixed oxides useful in the process of the present invention are characterized by a surface area of more than $500 \text{ m}^2/\text{g}$, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å. Their XRD spectrum from powders does not have a crystalline structure, does not show any peak, and optionally shows a

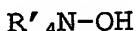


widespread scattering at angular value not greater than $2\theta = 5^\circ$, with $\text{CuK}\alpha$ radiation, while other scattering phenomena coherent for greater angular values are absent. In particular the completely amorphous micro-mesoporous mixed oxides, whose XRD spectrum from powders does not have a crystalline structure and does not show any peak, are called MSA type and the completely amorphous micro-mesoporous mixed oxides whose XRD spectrum from powders does not have a crystalline structure, does not show any peak, and shows a widespread scattering at angular value not greater than $2\theta = 5^\circ$, with $\text{CuK}\alpha$ radiation, while other scattering phenomena coherent for greater angular values are absent, are called ERS-8 type.

The micro-mesoporous completely amorphous mixed oxide of MSA type, useful in the process of the present invention, containing a matrix of an oxide (YO) selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides (MO) selected from transition metal oxides and group IVA metal oxides, preferably selected from the oxides of titanium, zinc, vanadium and tin, are

uniformly dispersed, can be prepared, besides the preparation described in EP 492697 and in EP 812804, also in the following way:

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolyzable compounds of Si, Al, Ce, Mg, or mixture thereof, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):



wherein R' represents a C₃-C₇ alkyl group and of one or more soluble or hydrolyzable compounds of one or more transition metals or group IVA metal, preferably selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

$$\text{alcohol/YO} = 5-20$$

$$\text{R}'_4\text{N-OH/YO} = 0.05-0.5;$$

$$\text{H}_2\text{O/YO} = 5-30$$

$$\text{YO/MO} \geq 5$$

whereas the ratio H₂O/R'₄N⁺ varies according to the number of carbon atoms in the R' alkyl chain, in accordance with the values shown in table A below :

Table A

R'	H ₂ O/R' ₄ N ⁺
Hexyl	> 133
Pentyl	> 100
5 Butyl	> 73
Propyl	> 53

operating at a temperature between the room temperature and the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying and calcinations.

The soluble or hydrolizable compounds of Si which can be used are tetra-alkyl orthosilicates selected from tetramethyl, tetraethyl, tetranormalpropyl, tetraisopropyl, tetranormalbutyl, tetrasecbutyl, 20 tetraterbutyl orthosilicate, and among these tetraethylorthosilicate is preferred. The soluble or hydrolizable compounds of Al which can be used are

aluminium trinormalpropoxide, triisopropoxide,
trinormalbutoxide, trisecbutoxide and triterbutoxide.
The soluble or hydrolyzable compounds of one or more
transition metals or group IVA metals, preferably
5 selected from Ti, V, Zr, Sn, can be selected from the
hydrosolubile or hydrolyzable salts or acids of the
metals themselves. Tetraethylorthotitanate is
preferred. The alcohol can be selected among C₂-C₆
alcohol and preferably is ethanol.

10 When the catalytic composition contains both silica and
alumina, in the step (a) of the preparation a soluble
or hydrolyzable compound of Si and a soluble or
hydrolyzable compound of Al are used, preferably in the
molar ratio SiO₂/Al₂O₃ ≥ 30.

15 When the catalytic composition also contain boron
and/or gallium oxides, in the step (a) of the
preparation one or more soluble or hydrolyzable
compounds of boron and/or gallium are added, in the
molar ratio between the oxide matrix and boron and/or
gallium oxide higher or equal to 5.

20 The micro-mesoporous amorphous mixed oxide of ERS-8
type, useful in the process of the present invention,

containing a matrix of a oxide (YO) selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides (MO) selected from transition metal oxides and group IVA metal 5 oxides, preferably selected from the oxides of titanium, zinc, vanadium and tin, are uniformly dispersed, can be prepared according with the above preparation wherein the ratios $H_2O/R'{}_4N^+$ varies according to the number of carbon atoms in the R' alkyl 10 chain , in accordance with the values shown in table B below :

Table B

R'	$H_2O/R'{}_4N^+$
Hexyl	≤ 133
Pentyl	≤ 100
Butyl	≤ 73
Propyl	≤ 53

A particularly preferred aspect of the invention is using completely amorphous micro-mesoporous mixed 15 oxides of MSA type consisting of a silica matrix 20 wherein one or more metal oxides are uniformly

dispersed, these being selected from the oxides of titanium, zirconium, vanadium, tin.

Another particularly preferred aspect of the invention is using completely amorphous micro-mesoporous mixed 5 oxides of MSA type consisting of a silica and alumina matrix wherein one or more metal oxides are uniformly dispersed, these being selected from the oxides of titanium, zirconium, vanadium, tin. They are new and a further object of the present invention.

10 A further particularly preferred aspect of the invention is using completely amorphous micro-mesoporous mixed oxides of ERS-8 type consisting of a matrix of silica or a matrix of silica and alumina, wherein one or more metal oxides are uniformly 15 dispersed selected from oxides of titanium, zinc, vanadium and tin.

Said mixed oxides, excluding the mixed oxides containing a silica matrix wherein titanium oxide is uniformly dispersed, are a selection from the 20 compositions described in EP 691305 and are new.

The completely amorphous micro-mesoporous mixed oxides used in the process of the present invention containing

an oxide matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides selected from oxides of Ti, V, Zr, Sn, are uniformly dispersed, excluding the mixed oxide of MSA
5 type containing a silica matrix wherein one or more metal oxides are uniformly dispersed selected from the oxides of titanium, zirconium, vanadium, tin and excluding the mixed oxide of ERS-8 type containing a silica matrix wherein titanium oxide is uniformly
10 dispersed, are new and are a further object of the present invention.

A further particularly preferred aspect of the invention is using all the above described catalytic compositions in silylated form.

15 When the catalyst is silylated and is used in the process for desulphurizing of the present invention best results are obtained with lower catalyst amount than the same catalyst in not silylated form.

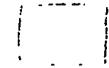
Therefore a particularly preferred aspect of the
20 invention is a process for desulphurizing hydrocarbons boiling within the range of 180° to 360°C, containing less than 350 ppm of sulphur as thiophenic compounds,



which comprises putting these mixtures in contact, in
the presence of an organic peroxide, with a
catalytic composition comprises a completely amorphous
microporous and/or mesoporous mixed oxide containing a
5 matrix selected from silica, alumina, ceria, magnesia
and mixtures of thereof, wherein one or more metal
oxides selected from the transition metal oxides and
group IVA metal oxides, preferably oxides of Ti, V, Zr,
Sn, are uniformly dispersed, whose surface has -O-
10 Si(R)₃ groups, wherein R can be the same or different
each other and are selected from C₁-C₄ alkyl, aryl,
preferably phenyl, polyaryl groups, that can contain
functional groups as acids, amines, thiols, sulfonics
or trialkylamines.

15 The obtained sulphur oxygenated products are then
separated from the hydrocarbon mixture.

The mixed oxides of the present invention have a molar
ratio between the metal oxide matrix and the dispersed
metal oxide between 5 and 300, and after silylation
20 higher than 5 and less or equal to 400, computing the
added Si as constituent of the matrix, expressed as
 SiO_2 .



The silylated mixed oxides of the present invention can optionally contain gallium and/or boron oxides.

When a silylated catalyst is used in the process of the present invention, it can be prepared using the above 5 described sol-gel procedure where in the step (b), after drying, the material is outgassed in vacuum and then a solution of the silylating agent in an organic solvent, as for instance toluene or dichloromethane, is added. The ratio of the silylating agent (SA) to the 10 metal (M), selected from transition metal and group IVA metal, is in the range from 0.05 to 1.0 moles of SA to mole of metal M. As silylating agent one can use for example hexaalkyldisilazane or hexaaryl disilazane. The alkyl or aryl groups of the disilazane can be selected 15 from C₁-C₄ alkyl, phenyl, and polyaryl groups, and they can contain functional groups as acids, amines, thiols, sulfonics or trialkylamines.

The resulting mixture is refluxed under inert atmosphere and then the silylated sample is filtered 20 and washed, for example with toluene. The obtained product is dried.

The completely amorphous micro and/or mesoporous mixed oxides containing a matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxide selected from 5 transition metal oxides and group IVA metal oxides, preferably selected from the oxides of Ti, V, Zr, Sn are uniformly dispersed, whose surface has $-O-Si(R)_3$ groups, wherein R can be the same or different each other, R being selected from alkyl, aryl and polyaryl groups that can contain functional groups as acids, 10 amines, thiols, sulfonics or tetraalkylammonics, are new and are a further aspect of the present invention. They can optionally contain boron and/or gallium oxides. According to a preferred aspect of the present 15 invention these catalytic composition are micro-mesoporous. They are characterized by a surface area of more than $300\text{ m}^2/\text{g}$, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, and their XRD spectrum do not show a crystalline 20 structure, but optionally a widespread "scattering" with angular values of not more than $2\theta=5^\circ$.

The catalysts used in the process of the present invention can be used as such or, preferably, extruded according to the known techniques, i.e. using a binder, as pseudobohemite, and a peptizing agent, as acetic acid solution, added to the catalyst to produce an extrudable paste.

The oxidative desulphurization process of the present invention can be carried out at a temperature ranging from 50 to 120°C, preferably from 60 to 90 °C. It can be carried out in presence of an organic peroxide with a molar ratio in respect to S lower than or equal to 30, preferably lower than or equal to 14. The higher values of the molar ratio ranges are suitable for the oxidative desulphurization of hydrocarbon mixtures also containing impurities or compounds that can react with the peroxide. According to the quantities of impurities or compounds that can react with the peroxide also higher molar ratio values can be used if necessary. A preferred aspect is using a molar ratio of organic peroxide in respect to S higher than or equal to 2, preferably ranging from 2 to 30, more preferably ranging from 2 to 14.



According to a particular aspect the oxidative desulphurization process of the present invention is carried out at a temperature ranging from 50 to 120°C, preferably at atmospheric pressure, in presence of an 5 organic peroxide with a weight ratio in respect to S ranging from 2 to 15.

The hydrotreated hydrocarbon mixtures which can be desulphurized according to the process of the present invention contain less than 350 ppm of sulphur. For 10 example hydrotreated hydrocarbon mixtures boiling in the diesel range of 180-360 °C with a sulphur content less than 350 ppm, can be subjected to oxidative desulphurization.

The hydrotreating hydrocarbon mixture which is 15 preferably subjected to oxidative desulphurization according to the process of the present invention consists of hydrocarbons boiling in the diesel range such as LCO.

The process of the present invention is carried in 20 unique organic phase and in absence of added solvent.

The sulphur compounds contained in the hydrocarbon mixtures of the process of the present invention are

thiophene compounds, in particular dibenzothiophene (DBT), alkylbenzothiophene (alkylDBT), polyalkylbenzothiophene (polyalkylDBT). At the end of the oxidative desulphurization process oxygenated sulphur products are obtained having higher polarity and/or molecular weight. They can be easily separated from the hydrocarbon mixtures, for example by distillation or by solvent extraction methods or by selective adsorption. The skilled person well knows how to carry out said methods. If it is done by solvent extraction, preferably the removal of sulphur oxygenated products from the treated hydrocarbon mixtures can be effected for example by extraction with methanol, acetonitrile, dioxane, methyl-terbutyl-ether. Alternatively the sulphur oxygenated products can be removed by distillation.

In the following examples catalysts preparations are reported, and tests performed either on a model feed or on a LCO cut.

20 EXAMPLE 1 (preparation of Ti-ERS-8)

1.34 g of $Ti(OCH_3)_4$ (TEOT) was dissolved at room temperature in 124.8 g of $Si(OC_2H_5)_4$ (Dynasil-A,

Nobel). The solution obtained was added to 143.8 g of tetrahexylammonium hydroxide (40 wt % THA-OH in aqueous solution - Fluka) and 220.8 g of EtOH (Molar ratio in reagent mixture: THA-OH/SiO₂=0.26, H₂O/SiO₂=8, 5 EtOH/SiO₂ = 8 and SiO₂/TiO₂ = 102).

The monophasic clear solution was heated at 50°C under stirring. After 2 hours a viscose transparent gel. The gel was dried at 120 °C 6 hours and calcined 8 hours in air at 550 °C to eliminate the organic gelling agent. 10 The obtained Ti-ERS-8 shows a SSA of 600 m²/g, with a pore volume of 0.31 ml/g , with a diameter of less than 40 Å. The XRD spectrum shows the presence of a widespread scattering in the angular region at 2θ of between 1° and 4°.

15 EXAMPLE 2-4 (preparation of Ti-MSA)

Samples were prepared via sol-gel using Si(OC₂H₅)₄ (Dynasil-A, Nobel), TEOT (Fluka), tetrapropylammonium hydroxide (TPAOH, Sachem), alcohol (EtOH). All preparations were performed at the same molar ratio: 20 TPAOH/SiO₂=0.09, H₂O/SiO₂=8, EtOH/SiO₂=8.

The molar ratio SiO₂/TiO₂ was changed between 20 and 100.

The synthesis preparation is following described: three different amount of TEOT (see Table 1) were dissolved in a solution of 104.2 g Si(OC₂H₅)₄ and 184 g EtOH. The obtained homogeneous solutions were added to 90 g TPA-OH aqueous solution (11.3 wt %). Monophasic clear solutions were obtained and, after 15-30 minutes under stirring at room temperature, transformed in homogeneous compact gels without separation of phases. Table 1 shows the gelling time related to the SiO₂/TiO₂ molar ratio.

After 16 hour ageing at room temperature, the gels were dried at 120 °C for 7h.

In order to decompose and eliminate the gelling agent the dried gels were calcined 8h in air at 550 °C.

15

Table 1

	TEOT (g)	Molar ratio SiO ₂ /TiO ₂	Gelling time (min)
EXAMPLE 2	6.00	20	28
EXAMPLE 3	2.98	39	18
EXAMPLE 4	1.16	100	15

The textural properties of calcined samples were determined by nitrogen isotherms at liquid N₂ temperature, using a Micromeritics ASAP 2010 apparatus

(static volumetric technique). Before determination of adsorption-desorption isotherms the samples (~ 0.2 g) were outgassed for 16 h at 350 °C under vacuum.

The specific surface area (SSA) was evaluated by 2-
5 parameters linear BET plot in the range p/p° 0.01-0.2. The total pore volume (VT) was evaluated by Gurvitsch rule. Medium pore size (dDFT) and pore size distributions were calculated using DFT method for all materials.

10 Ti-MSA described in EXAMPLE 2-4 show the textural properties reported in the following Tab. 2:

Table 2

	SSA (m ² /g)	Vpore (ml/g)	D medium (DFT) nm
EXAMPLE 2	820	0.54	2.4
EXAMPLE 3	820	0.56	2.5
EXAMPLE 4	790	0.72	3.7

The Ti-MSA described in EXAMPLE 2-4 have XRD spectra from powders that do not show any peak, as described on page. 11. Ti-MSA described in EXAMPLE 2-4 show the UV-Vis profiles reported in figure 1.

UltraViolet-Visible (UV-Vis) spectroscopic analysis of powdered samples was performed with a Perkin-Elmer 20 Lambda 19 spectrophotometer, equipped with a reflectance sphere. The spectra were registered at

295 K with 1 nm resolution in 190-500 nm range, in Kubelka-Munk resolution (KM).

UV-Vis spectroscopy gives information about coordination of Ti atoms. The band in the range 190-
5 210 nm is attributed to the charge transfer of Ti (Td) sites, while segregated TiO_2 (Oh) absorbs at 310-
330 nm [M. Padovan, F. Genoni, G. Leofanti, G. Petrini, G. Trezzi and A. Zecchina, in "Preparation
of Catalyst V", G. Poncelet, P.A. Jacobs, P. Grange
and B. Delmon Eds., (1991) 431]; absorptions at 238-
10 and 330 nm are attributed to atomically dispersed Ti atoms in octahedral coordination with oxygen ligands
[J. Weitkamp, S. Ernst, E. Roland and G.F. Thiele,
Stud. Surf. Sci. Catal. 105 (1997) 763] or to Ti agglomerates (via oxygen-bridges) giving TiO_2 clusters
15 of increasing sizes [J. Weitkamp, S. Ernst, E. Roland and G.F. Thiele, Stud. Surf. Sci. Catal. 105 (1997)
763].

EXAMPLE 5 (silylated Ti-MSA)

20 In this example the catalyst of example 2, in not calcined form, has been activated with a silylation procedure described as following: 2.0 g of the solid was

outgassed in vacuum (10^{-3} torr) at 100 °C during 2 hours. Then, the sample was cooled and 1.88 g. of hexamethyldisilazane in 30 g. of toluene solution were added under Argon. The resulting mixture was refluxed 5 at 120 °C during 90 minutes under inert atmosphere, and then the silylated sample was filtered and washed with toluene.

The obtained silylated Ti-MSA shows the textural properties reported in the following Tab. 3.

10 EXAMPLE 6 (silylated Ti-MSA)

In this example the catalyst of example 3, in not calcinated form, has been activated with a silylation procedure as described in example 5. The obtained silylated Ti-MSA shows the textural properties reported 15 in the following Tab. 3.

EXAMPLE 7 (silylated Ti-MSA)

In this example the catalyst of example 4, in not calcinated form, has been activated with a silylation procedure as described in example 5. The obtained 20 silylated Ti-MSA shows the textural properties reported in the following Tab. 3.

Table 3



Catalyst	Si / Ti	SSA (m ² /gr)	Vpore (ml/g)	Pore width (nm)	C content (%wt.)
EXAMPLE 5	21	578.7	0.43	2.3	5.313
EXAMPLE 6	38	576.3	0.47	2.4	5.756
EXAMPLE 7	114	526.9	0.51	3.5	5.591

EXAMPLE 8

In this example the test with the catalyst of example 1 is described. The same procedure is applied in the 5 following examples, except when specified.

The test was carried out in a 25-50 ml. round-bottom flask immersed in a thermostated bath and equipped with a condenser, thermometer and a magnetic stirrer. A mixture of 0.2g. of terbutylhydroperoxide 10 (TBHP) with 10g. of hydrocarbon solution (containing a mixture of model organic sulphur compounds) and 0.075 g. of n-decane as internal standard was homogenised in the flask under stirring and heating at constant temperature (80°C). Then, 0.2g of 15 catalyst were added at once to the reaction mixture (time zero). Small aliquots were carefully withdrawn from the mixture at time intervals to follow the kinetic of the reaction. The reaction products were analysed by gas chromatography in a Varian 3400 GC

equipped with a capillary column (5% methyl-phenylsilicone, 25 m. length) and a FID. Product identification was performed by GC-MS and available standard compounds.

5 In Table 4 the model feed components are reported:

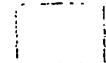
10

	Component	%w/w in the mixture	S in the mixture (ppm)
Hydrocarbons	Aromatics	20	-
	Olefins	12	
	Parafins	68	-
Sulphur Compounds	Thiophene		60
	2 Methyl-thiophene		60
	Di-methyl-thiophene		30
	Benzothiophene		60

15

Table 4

The catalytic results are reported in the following table 5.



EXAMPLE 9 (comparative)

In this example the test performed with the catalyst of example 1 is reported, following the procedure of example 8 a part for the oxidant chosen that is H₂O₂.

5 Results are reported in Table 5.

EXAMPLE 10

In this example the test performed with the catalyst of example 4 is reported, following the procedure of example 8. Results are reported in the following Table

10 5 :

Table 5

Components	S content	S Conversion % EX.8	S Conversion % EX.9 (comparative)	S Conversion % EX.10
Thiophene	60 ppm	11	3	10
2-Me-Thioph.	60 ppm	24	2	18
Di-Me-Thioph.	30 ppm	59	3	31
Benzothiophene	60 ppm	99	10	92
S Total (ppm)	210 ppm	111 ppm	200 ppm	129 ppm

EXAMPLE 11

The tests were performed with the catalyst of example 4, following the procedure of example 8, with the feed of Table 6. The tests were performed changing the amount of catalyst. Results are reported in Table 7, where the different catalyst amount are reported.

Table 6

	Component	%w/w in the mixture	S in the mixture (ppm)
Hydrocarbons	Aromatics	20.00	-
	Parafins	79.98	-
Sulphur Compounds	Benzothiophene		80
	Methyl-Benzothiophene		60
	DiBenzothiophene		60

EXAMPLE 12

In this example the tests performed with the catalysts of example 7 are reported, following the procedure of example 11. Results are reported in Table 7:

TABLE 7

S Ppm	Cat. ex. 4	S conv. % with		S conv. % with	
		0.1 cat. %w	0.3 cat. %w	0.1 cat. %w	0.3 cat. %w
BT	80	71.2	87.3	84.7	95.8
Me-BT	60	80.1	91.8	92.4	98.3

DBT	60	100.0	100.0	100.0	100.0
		83.8	93.0	92.4	98.0
S (ppm)	200	(32 ppm)	(14 ppm)	(15 ppm)	(4 ppm)

EXAMPLE 13

In this example the tests performed with the catalysts of examples 2 and 5 are reported, following the 5 procedure of example 11. Results are reported in Table 8:

Table 8

S ppm	S conv. % with Cat. EX. 2		S conv. % with Cat. EX. 5	
	0.1 cat. %w	0.3 cat. %w	0.1 cat. %w	0.3 cat. %w
	BT	80	95.6	99.0
Me-BT	60	71.1	90.9	100.0
DBT	60	95.3	100.0	100.0
S (ppm)	200	77.2 (46 ppm)	92.1 (16 ppm)	99.7 (1 ppm)

EXAMPLE 14

10 In this example the tests performed with the catalysts of examples 3 and 6 are reported, following the procedure of example 8. Results are reported in Table 9:

Table 9

S ppm	S conv. % with cat. EX. 3 (Ti-MSA-Cat)		S conv. % with cat. EX. 6 (Ti-MSA silylated)	
	0.1 cat %w	0.3 cat %w	0.1 cat %w	0.3 cat %w
BT	80	98.2	98.3	100.0
Me-BT	60	97.8	100.0	100.0
DBT	60	100.0	100.0	100.0
S (ppm)	200	98.7 (3 ppm)	99.4 (1 ppm)	100.0 (0 ppm)

EXAMPLE 15

The test were performed with the catalysts of example 2
 5 and 3 and of example 5 and 6 (after silylation procedure) using a real LCO feed, following the procedure as below.

The experiments of oxidation of sulphur containing compounds were carried out in a 25-50 ml. round-bottom flask immersed in a thermostated bath and equipped with a condenser, thermometer and a magnetic stirrer. Typically, a mixture of 0.05g. of TBHP with 10 15g. of LCO with sulphur containing compounds and 0.075g. of n-decane as internal standard was 15 homogenised in the flask under stirring and heating

at constant temperature (80°C). Then, 0.055 of catalyst were added at once to the reaction mixture (time zero). Small aliquots were carefully withdrawn from the mixture at time intervals to follow the kinetic of the reaction. The reaction mixtures were analysed by gas chromatography in a Varian 3400-GC equipped with a Petrocol-100 fused silica column connected to two detectors (FID and PFPD) in parallel at the outlet of the column. Results are reported in table 10.

Table 10

Components	S (ppm)	Conversion			
		Ti-MSA		Ti-MSA-Silylated	
		Cat. EX. 2	Cat. EX. 3	Cat. EX. 5	Cat. EX. 6
DBT	0	-	-	-	-
Alkyl-DBT's	18	100.0	100.0	100.0	100.0
Di-alkyl-DBT's	58	54.0	81.5	68.0	93.9
Poly-alkyl-DBT's	164	96.0	95.2	97.4	99.3
S ppm	200	87.2 (31ppm)	92.0 (20ppm)	91.3 (22ppm)	97.9 (5ppm)